



TITLE:

Research upon Joint Reaction and Transjointing. (IV)

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Research upon Joint Reaction and Transjointing. (IV)

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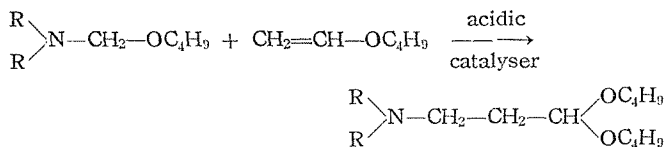
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Continued from the previous report,¹⁾ the authors have performed the following re-searches upon Transjointing Reactions.

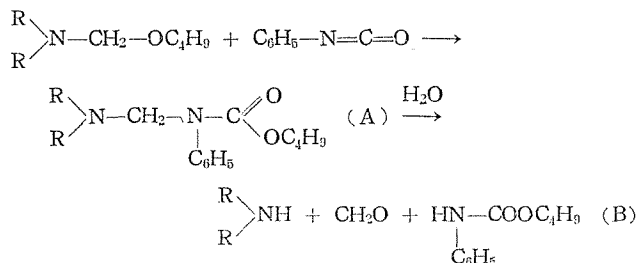
- (1) Transjointing between dialkylaminomethyl alkyl ether and phenylisocyanate.
- (2) Transjointing between Mannich Base and phenylisocyanate.
- (3) Transjointing between dialkylaminomethyl alkyl ether and ketene.
- (4) Transjointing between dialkylaminomethyl alkyl ether and ethylene oxide.
- (5) Transjointing between dialkylaminomethyl alkyl ether and styrene.
- (6) Transjointing between chloromethyl alkyl ether and phenylisocyanate.
- (7) Transjointing between sulfomethylbenzamide and some other components.

(1) TRANSJOINTING BETWEEN DIALKYLAMINOMETHYL ALKYL ETHER AND PHENYLISOCYANATE

In the previous report¹⁾ the authors found that dialkylaminomethyl *n*-butyl ether (jointed compound of dialkylamine and alcohol by formaldehyde) reacted with *n*-butyl vinyl ether in the following manner :



The authors then expected that the analogous Transjointing Reaction should occur between the dialkylaminomethyl butyl ether and phenylisocyanate in the following manner :



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The authors have ascertained that this reaction indeed occurs, but the reaction product (A) is unstable and easily hydrolyzed in (B), *i. e.*, butyl phenylcarbamate. As the dialkylamine diethylamine and morpholine were used.

Dialkylaminomethyl alkyl ethers and methylene-bis-dialkylamines, which were used in this and the following experiments, were prepared after the method of T. D. Stewart,²⁾ and characteristics of these compounds are given in the following table.

	bp.	°C/mm	Neutralization equivalent	
			Found	Calcd.
$(C_2H_5)_2N-CH_2-OC_2H_5$	131.5~132.5°	760	130.5	131.0
$(C_2H_5)_2N-CH_2-OC_4H_9$	71~72°	18	157.5	159.0
$O\langle\rangle N-CH_2-OC_4H_9$	104.5~107°	18	170.0	173.0
$\langle\rangle N-CH_2-OC_4H_9$	103~105°	20	166.0	171.0
$(C_2H_5)_2N-CH_2-N(C_2H_5)_2$	166~168°	760	78.0	79.0
$O\langle\rangle N-CH_2-N\langle\rangle O$	129~132°	12	94.0	93.0
$\langle\rangle N-CH_2-N\langle\rangle$	100.6°	12	90.6	91.0

An example of the experiment is as follows: When diethylaminomethyl butyl ether and phenylisocyanate were mixed in equimolecular ratio, an exothermic reaction took place, but the product was only the trimer of phenylisocyanate, that is the polymerization of phenylisocyanate was induced by the other component. But, when both the components were mixed in the presence of anhydrous $ZnCl_2$ (1 g $ZnCl_2$ for 0.1 mole of each component), an exothermic reaction also occurred, but the mixture become soon reddish brown and viscous. This reaction product was distilled in vacuum and the following two fractions were obtained.

(i) 60~105°/25 mm, 6 g.

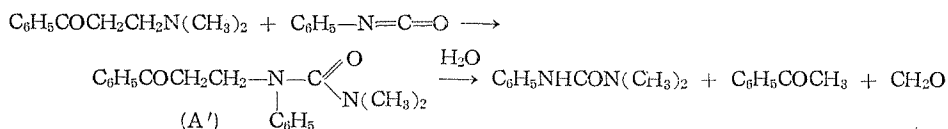
(ii) 135~148°/5 mm, 14 g.

The second fraction (1.386 g) was dissolved in a small quantity of ethanol, 5 cc conc. HCl was added and then heated for 2 hours on a water-bath. The acidic solution was extracted with ether and from the ether extract 0.888 g butyl phenylcarbamate was obtained. From the residual acidic solution 0.361 g diethylamine hydrochloride was recovered after evaporation. Both products were identified respectively comparing with authentic samples, and the yields were calculated from the above data as 92.3 and 94.6 %, respectively. The product before hydrolyzing *i. e.*, the fraction (ii) is unstable and decomposes slowly splitting off formaldehyde.

The reaction between morpholinomethyl butyl ether and phenylisocyanate was performed in the same manner as the above. The fraction 147~162°/4 mm was hydrolyzed with HCl, and butyl phenylcarbamate and morpholine hydrochloride were obtained in 96.3 % and 87.1 % yield, respectively.

(2) TRANSJOINTING BETWEEN MANNICH BASE
AND PHENYLISOCYANATE

As a Mannich Base β -dimethylaminopropiophenone was chosen and the following reaction was ascertained.

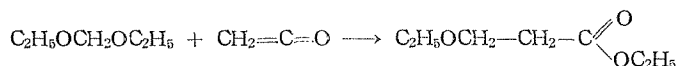


A vigorous reaction occurred when both the components were mixed without any catalyser and the reaction mass solidified. This product was washed with benzene in order to remove the unreacted components and dissolved in ethanol. A small quantity of alcohol-insoluble matter (this was identified as the trimer of phenylisocyanate) was removed by filtration and from the filtrate the alcohol was evaporated. There remained a white crystal (mp. 118–125°) and this was recrystallized from water and analyzed. mp. 130–134°; C, 66.67 %; H, 7.20 %; N, 16.66%. These values coincide well with those of N-phenyl-N'-dimethylurea (calcd. for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}$: C, 66.90 %; H, 7.31 %; N, 17.10 %; mp. 134°).

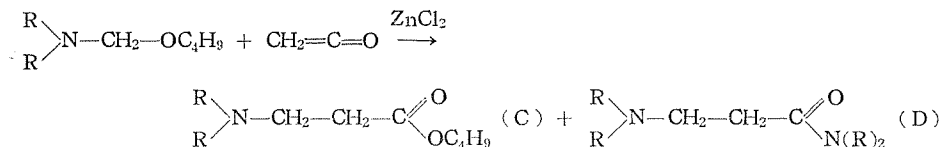
In this case the intermediate product, given above in [A'], was also unstable and could not be identified as itself.

(3) TRANSJOINTING BETWEEN DIALKYLAMINOMETHYL
ALKYL ETHER AND KETENE

It is already known that diethylformal (jointed compound of two molecules of ethanol by formaldehyde) reacts with ketene in the presence of acidic catalyser in the following manner³⁾:

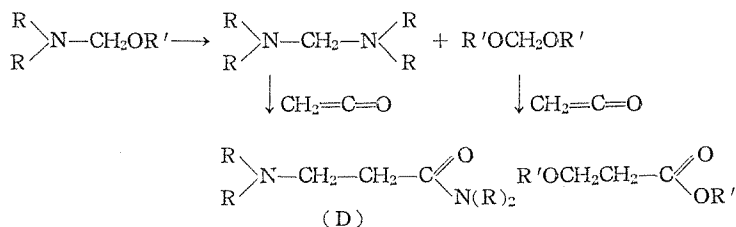


The authors expected that the analogous Transjointing Reaction should occur also between the dialkylaminomethyl alkyl ether and ketene and ascertained that this expectation is correct.



As the reaction product β -dialkylaminopropionamide (D) was detected together with β -dialkylaminopropionic ester (C). It is not clear at present, through which course (D) was formed, but one possibility may be as follows:

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Therefore, the authors examined the Transjointing reaction between methylene-bis-amine and ketene and ascertained that (D) is obtained in good yield also in this case.

(i) **Reaction between diethylaminomethyl ethyl ether and ketene.** In a four-necked flask, equipped with a stirrer, a thermometer, a CaCl_2 -tube and an inlet-tube of ketene, 0.3 mole of diethylaminomethyl ethyl ether was dissolved in 70 ml absolute ether, and under stirring and cooling with ice-salt mixture 47 g (0.35 mole) anhydrous ZnCl_2 was added. Next ketene was introduced slowly maintaining the temperature at $4\sim 6^\circ$. The ketene was prepared by the pyrolysis of acetone and introduced directly into the reaction flask, after passing a trap cooled with ice-salt mixture to remove the unreacted acetone.

After about 35 minutes, when the reaction solution became yellow and the temperature began to drop, the ketene introduction was stopped and the reaction solution was stored overnight. Then this was poured into 220 ml of 15% NH_4OH solution, the oily layer was separated and the aqueous layer was extracted three times with ether. The oily product and the ether extract were joined together, dried and distilled. The following two fractions were collected.

(i) $47\sim 79^\circ/9\text{ mm}$, 5 g

(ii) $98\sim 113^\circ/7\text{ mm}$, 10.5 g.

The first fraction was dissolved in dil. HCl , washed with ether in order to remove some amount of HCl -insoluble oily matter and made alkaline with soda. The separated free amine was extracted with ether, dried and distilled. The fraction, boiling at $75\sim 76^\circ/11.5\text{ mm}$ was obtained in 2.5 g yield. The boiling point is lower than that of ethyl β -diethylaminopropionate ($83\sim 84^\circ/12\text{ mm}$), but the result of elemental analysis coincides well with the calculated value of it. Further this product was converted into the methiodide. The mp. of this methiodide is $77\sim 81^\circ$ (literature: $80\sim 81^\circ$).

Found: C, 38.14 %; H, 7.25 %; N, 4.07 %.

Calcd. for $\text{C}_{10}\text{H}_{22}\text{NO}_2$: C, 38.09 %; H, 7.00 %; N, 4.44 %.

The second fraction was redistilled and the main part distilled out at $103\sim 106^\circ/6\text{ mm}$. Its neutralization equivalent was found as 197 (calculated 201) and its picrate (mp. $68\sim 71^\circ$) was analysed.

Found: C, 47.39 %; H, 6.31 %; N, 16.33 %.

Table 1.

Ethers	Product (C)						Product (D)					
	bp. °C/mm	Yield ^a (%)	Anal. ^c			NE ^a	bp. °C/mm	Yield ^d (%)	Anal. ^e			NE ^a
			C (%)	H (%)	N (%)				C (%)	H (%)	N (%)	
$(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{OC}_2\text{H}_5$	75~76° /11.5	9.72	62.38 (62.43)	11.13 (10.98)	7.91 (8.09)	172.6 (173)	103°~106° /6.0	35.2	—	—	—	197
$(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{OC}_4\text{H}_9$	93.5~ 94.5°/8	9.95	65.35 (65.67)	11.79 (11.44)	6.91 (6.96)	205.9 (201)	103~ 105°/6.0	20.0	—	—	—	—
$\text{O} \begin{array}{c} \diagup \diagdown \\ \text{N} \end{array} \text{—CH}_2\text{OC}_4\text{H}_9$	117~118° /10	14.0	61.67 (61.40)	9.93 (9.77)	7.25 (6.51)	—	(89~93°) ^b	3.5	57.62 (57.89)	8.70 (8.77)	12.34 (12.28)	—
$\begin{array}{c} \diagup \diagdown \\ \text{N} \end{array} \text{—CH}_2\text{OC}_4\text{H}_9$	101~ 102°/5.5	18.8	67.09 (67.61)	10.73 (10.80)	6.65 (6.57)	—	(37~41°) ^b	53.6	69.25 (69.64)	11.18 (10.71)	12.56 (12.50)	—

^a Neutralization equivalent^b Melting point.^c All the values given in the parenthesis are the calculated.^d Yield is the crude yield on the aminomethylether.^e The product (D) was analyzed as its picrate in the first two cases, and as itself in the last two cases.

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Calcd. for $C_{13}H_{18}N_4O_9$: C, 47.55 %; H, 6.29 %; N, 16.32 %.

This product was next hydrolyzed refluxing with dil. HCl for 2.5 hours. From the hydrolyzate diethylamine hydrochloride and β -diethylaminopropionic acid were isolated. The former was identified by mixed melting point determination with an authentic sample, and the latter was converted into the hydrochloride (mp. 130~136°) analyzed.

Found: C, 44.19 %; H, 9.08 %; N, 7.12 %.

Calcd. for $C_7H_{16}NO_2Cl$: C, 46.28 %; H, 8.82 %; N, 7.71 %.

From these results it is clear that the second fraction is β -diethylaminopropionic diethylamide.

The oily product which is obtained as HCl-insoluble part from the fraction (i) boils at 70~71°/17.5 mm and this may be ethyl β -ethoxypropionate, though precise identification is omitted.

The results obtained with other components are summerized in Table 1.

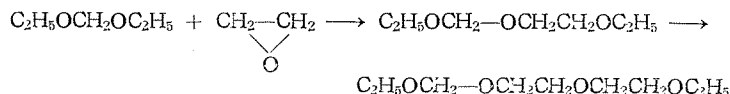
(ii) **Reaction between methylene-bis-amine and ketene.** The experimental procedure is the same as the preceeding section, except that $ZnCl_2$ was used in this case in a larger quantity (2.5 moles for 1 mole of the components). The products were identified by comparing with the products obtained above and the results are summerized in the following table.

Table 2.

R_2N-	Product	$\begin{array}{c} R \\ \diagup \\ N-CH_2CH_2-CON \\ \diagdown \\ R \end{array}$		
	bp. °C/mm	mp.	Yield (%)	
$(C_2H_5)_2N-$	103~106°/6	—	40.0	
$O\text{---}\text{C}_6\text{H}_4\text{---}N-$	187~189°/7.5	89-95°	57.9	
$\text{C}_6\text{H}_5\text{---}N-$	148~155°/7	37-42°	77.4	

(4) TRANSJOINTING BETWEEN DIALKYLAMINOMETHYL
ALKYL ETHER AND ETHYLENE OXIDE

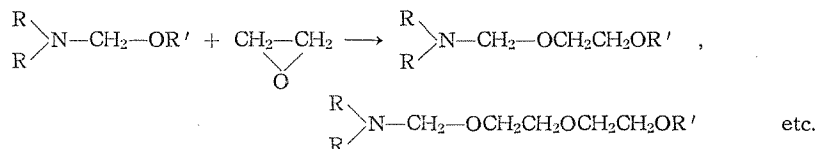
It is already known that diethylformal reacts with ethylene oxide in the presence of acidic catalyser in the following manner¹⁾:



This reaction is a kind of Transjointing and at the same time is a kind of ionic telomerization.

The authors expected that the analogous reaction should occur also between

the dialkylaminomethyl alkyl ether and ethylene oxide in the following manner and found that this was indeed the case.



In a four-necked flask, equipped with a stirrer, a thermometer, a CaCl_2 -tube and an inlet tube, 160 g diethylaminomethyl butyl ether and 26 g ethylene oxide were mixed and about 106 g BF_3 gas was introduced into this mixture, taking care that the temperature does not exceed 10° . After the saturation of BF_3 in the mixture the content of the flask was stirred 30 hours at room temperature and then poured slowly into 30 % NaOH solution. This alkaline solution was extracted with ether and the ether solution was dried and evaporated, the residue was distilled under vacuum and the fraction $80\sim 140^\circ/6.8\text{ mm}$ was collected. The crude distillate was rectified and the following two fractions were obtained.

(i) $82\sim 84^\circ/3\text{ mm}$, 4 g.

(ii) $108\sim 109^\circ/6.5\text{ mm}$, 2 g.

The fraction (i) was further purified with metallic Na and rectified ($76.5\sim 77^\circ/6\text{ mm}$) and analyzed.

Found: C, 64.63 %; H, 12.22 %; N, 6.40 %.

Calcd. for $\text{C}_{11}\text{H}_{25}\text{NO}_2$:

C, 65.02 %; H, 12.31 %; N, 6.90 %.

The second fraction was redistilled ($116^\circ/6\text{ mm}$) and analyzed.

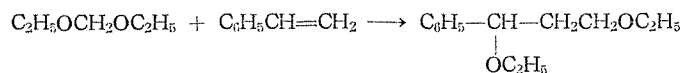
Found: C 62.93 %; H 11.68 %; N 5.94 %; NE 238.

Calcd. for $\text{C}_{13}\text{H}_{29}\text{NO}_3$:

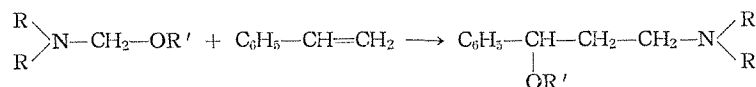
C, 63.16 %; H, 11.74 %; N, 5.67 %; NE 247.

(5) TRANSJOINTING BETWEEN DIALKYLAMINOMETHYL ALKYL ETHER AND STYRENE

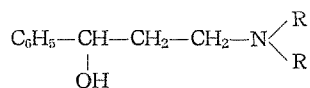
It is already known that diethylformal reacts with styrene in the presence of acidic catalyser in the following manner:⁵⁾



The authors expected that the analogous Transjointing Reaction should occur also between dialkylaminomethyl alkyl ether and styrene in the following manner and found that this was indeed the case.



But, as the actual reaction product, the hydrolyzed product was obtained.

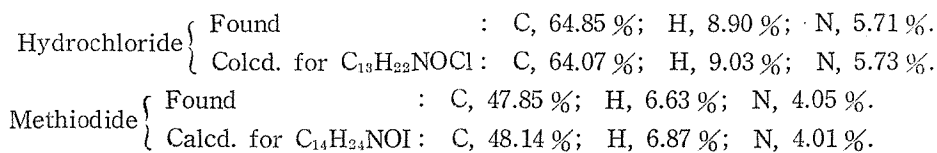


The experimental procedure is the same as the preceeding section and the results are summerized in the following table.

Table 3.

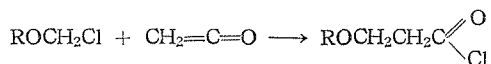
$(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{OBu}$ (g)	Styrene (g)	BF_3 (g)	Crude yield (g)	Residue (g)
16	10	5	1	
32	10	25	5	5
48	16	30	5	13
64	21	48	12	17

The product was rectified twice ($83\sim 87^\circ/7\text{ mm}$) and analyzed as the hydrochloride or methiodide.

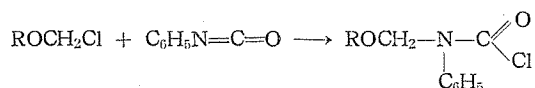


(6) TRANSJOINTING BETWEEN CHLOROMETHYL ALKYL ETHER AND PHENYLISOCYANATE

It is already known that chloromethyl alkyl ether (jointed compound of alcohol with hydrochloric acid by formaldehyde) reacts with ketene in the following manner⁶⁾ :



The authors expected that the analogous Transjointing Reaction should occur also between the chloromethyl alkyl ether and phenylisocyanate in the following manner and found that this was indeed the case.



In a four-necked flask, equipped with a stirrer, a thermometer, a CaCl_2 -tube and a dropping funnel, 0.1 mole chloromethyl alkyl ether, 40 ml absolute ether and anhydrous ZnCl_2 were mixed and the ethereal solution of phenylisocyanate (0.1 mole in

ca. 30 ml ether) was added, maintaining the temperature at 3~7°. After the addition of the phenylisocyanate solution the reaction mixture was stirred for 1 hr. and stood overnight at room temperature. Then, the ether was evaporated and the residue was distilled under vacuum. The results are summerized in the following table.

Table 4.

C_6H_5NCO (g)	$ClCH_2OR$ -R	(g)	$ZnCl_2$ (g)	bp. °C/mm	Yield (g)
12	-CH ₃	8.5	0.2	115~120°/6	5
12	-CH ₃	8.5	1	120~125°/7.0	4
12	-C ₂ H ₅	9.5	0.5	121~123°/5.5	4.5
12	-C ₄ H ₉	12.5	0.5	137~143°/6.0	4.0
12	-C ₆ H ₅	12.5	0.5	128~143°/6.0	4

The distilled products decompose easily splitting off hydrogen chloride and convert into reddish tarry matter even at room temperature and in closed vessel.

Therefore, the Cl- and N-content of the products were analyzed immediately after redistillation. The results are as follows:

Table 5.

C_6H_5NCOCl CH_2OR		Anal.			
-R	bp. °C/mm	N(%)		Cl(%)	
		Found	Calcd.	Found	Calcd.
-CH ₃	113 ~ 115°/5.0	6.31	7.02	18.41	17.76
-C ₂ H ₅	116 ~ 117°/4.5	5.99	6.56	16.45	16.63
-C ₄ H ₉	131 ~ 134°/6.0	5.56	5.80	17.33	14.70

As mentioned above, the distilled products are unstable and therefore these products were converted into more stable anilides. But instead of the expected $C_6H_5N-CONHC_6H_5$, N,N'-diphenylurea was obtained.

CH_2OR

For example, 2 g of C_6H_5NCOCl was dissolved in ether and to this solution 2 g CH_2OCH_3

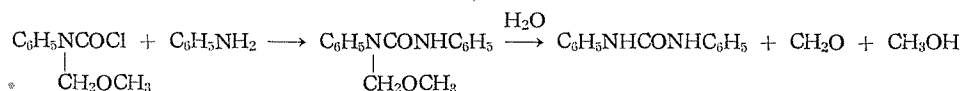
aniline was added. After removal of aniline hydrochloride by filtration, the ether was evaporated from the filtrate. The residue was a colorless solid and recrystallized twice from ethanol and analyzed.

Found: C, 73.20 %; H, 5.59 %; N, 13.18 %.

Calcd. for $C_{13}H_{12}O$:

C, 73.63 %; H, 5.66 %; N, 13.21 %.

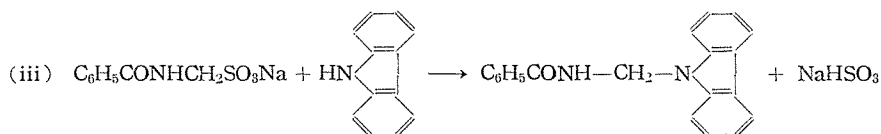
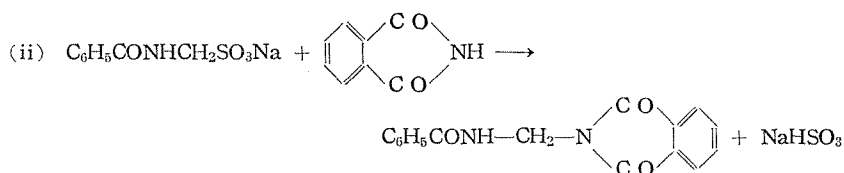
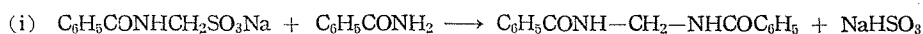
The mixed melting point measurement with an authentic sample exhibits no depression. From this result it may be concluded that the original compound changed during the treatment with aniline or recrystallization in the following manner:



This kind of change is reasonable from the fact that N,N' -diphenylurea is difficult to methylolize with formaldehyde.

(7) TRANSJOINTING BETWEEN SULFOMETHYLBENZAMIDE AND SOME OTHER COMPONENTS

The following three experiments were performed.



The starting material (sulfomethylbenzamide) was prepared by heating a mixture of 36 g benzamide and 80 g formaldehyde-bisulfite addition compound in a porcelain dish at $180\sim 190^\circ$ for 30 minutes. This crude material was recrystallized several times from water and finally from 60~70 % alcohol. The yield of the purified product was 37.5 g and the analysis is as follows:

Found : N, 5.60 %; Na, 9.32 %.

Calcd. for $\text{C}_8\text{H}_8\text{NO}_4\text{SNa}$: N, 5.91 %; Na, 9.70 %.

The Transjointing reaction was performed, for example, in the following manner. In a three-necked flask, 1 g metallic Na was dissolved in a small quantity of absolute methanol, 18 g benzamide and 7 g sulfomethylbenzamide were added and this mixture was heated gradually up to $190\sim 200^\circ$ in an oil bath, and during the heating methanol was evaporated. After heating at this temperature for 5.5 hrs. the reaction mass was cooled and unreacted materials were extracted with

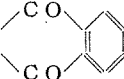

about 100 ml hot water. The water-insoluble residue was about 6.3 g. This crude product was recrystallized three times from hot alcohol. The mp. of the final product was 219~219.5° and it was identified as the methylene-bis-benzamide by mixed melting with an authentic sample and also by analysis.

Found : C, 70.75 % ; H, 5.73 % ; N, 10.95 %.

Calcd. for $C_{16}H_{14}N_2O_2$: C, 70.80 % ; H, 5.55 % ; N, 11.00 %.

The Transjointing between sulfomethylbenzamide and phthalimide or carbazole were performed analogously. As for the removal of the unreacted phthalimide or carbazole from the reaction product, both were converted into more soluble N-methylol derivatives and extracted with water. The results are given in the following table.

Table 6.

	Crude yield (%)	mp.		Anal.		
				C (%)	H (%)	N (%)
$C_6H_5CONHCH_2-N$ 	51	183~184°	Found	68.24	4.49	9.72
			Calcd.	68.55	4.32	10.00
$C_6H_5CONHCH_2-N$ 	49	199~199.5°	Found	79.70	5.53	9.53
			Calcd.	79.98	5.37	9.33

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